PART ONE
ESTERS OF GEOMETRICALLY ISOMERIC VINYL ALCOHOLS

PART TWO
THE ADDITION OF GRIGNARD REAGENTS TO AN OLEFINIC HYDROCARBON

BY

HERSCHEL DONOVAN PORTER

B. S., Wilmington College, 1944

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Professor Reynold C. Fuson for his suggestions and encouragement during the course of these investigations.

He is also indebted to the Rohm and Haas Company for the research assistantship held by him during 1946-1947.

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PART ONE

ESTERS OF GEOMETRICALLY ISOMERIC VINYL ALCOHOLS

Introduction

Geometrically isomeric acetates of 1,2-dimesityl-2-phenylvinyl alcohol have been prepared.[1] The direct esterification of the vinyl alcohol produced an acetate that was isomeric to that produced by the reaction of acetyl chloride with the intermediate formed from mesitylphenylketene and mesitylmagnesium bromide. Hydrolysis of each of the isomeric esters produced the same vinyl alcohol. This investigation is concerned with the esters of similar triarylvinyl alcohols. Also, the cleavage of the isomeric acetates of 1,2-dimesityl-2-phenylvinyl alcohol by means of the Grignard reagent was investigated in the hope that this method would produce both of the geometrically isomeric forms of the parent vinyl alcohol.

Discussion of Results

The reaction of triisopropylphenylmagnesium bromide with mesitylphenylketene, followed by subsequent hydrolysis, produced 1-tipyl-2-mesityl-2-phenylvinyl alcohol. The acetate prepared by the direct esterification of this vinyl alcohol by means of acetic anhydride and pyridine was shown to be identical with the acetate prepared by the reaction of acetyl chloride with the addition product from the ketene and Grignard reagent.

1-Isoduryl-2-mesityl-2-phenylvinyl alcohol was prepared in an analogous manner from mesitylphenylketene and isodurylmagnesium bromide. Again, the acetate prepared by the direct esterification of the vinyl alcohol was found to be identical with the acetate prepared from acetyl chloride and the ketene-Grignard adduct.

The hydrolysis of the above esters produced the parent vinyl alcohol.

Methods entirely analogous to those utilized in the preparation of the isomeric acetates were found to produce isomeric propionates of 1,2-dimesityl-2-phenylvinyl alcohol.

The cleavage of each of the isomeric acetates of 1,2-dimesityl-2-phenylvinyl alcohol by means of methylmagnesium iodide produced the same enolate and the same vinyl alcohol. This was shown by the reaction of the enolate so produced with propionyl chloride. The high-melting propionate was formed in each case. Since the enolate formed from the Grignard reagent and mesitylphenylketene produced a low melting propionate, it is to be concluded that the enolates are geometrical isomers as well as the esters.

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PART TWO

THE ADDITION OF GRIGNARD REAGENTS TO AN OLEFINIC HYDROCARBON

Introduction

The consideration of the known addition reactions of the olefinic double bond indicates that increasing conjugation with aromatic substituents renders such a carbon carbon double bond more susceptible to attack by neucleophilic reagents. The reported additions of amines[1] and of active hydrogen compounds[2] to bidiphenyleneethylene support this observation. Attempts to bring about the addition of Grignard reagents to the olefinic double bond have been fruitless.[3] The few cases in which such an addition apparently had occurred

have now been shown to be erroneous.[4]

Since the more reactive organometallic compounds are known to undergo addition to conjugated olefinic hydrocarbons,[5] it is to be expected that the more reactive Grignard reagents[6] such as *t*-butylmagnesium chloride and benzylmagnesium chloride would also be suitable for such an addition.

Discussion of Results

Bidiphenyleneethylene was found to add the more reactive Grignard reagents such as *t*-butylmagnesium chloride, benzylmagnesium chloride and *p*-chlorobenzylmagnesium chloride. The intermediate adduct behaved as a Grignard reagent toward water; 1-*t*-butyl-1,2-bidiphenyleneethane, 1-benzyl-1,2-bidiphenyleneethane, and 1-*p*-chlorobenzyl-1,2-bidiphenyleneethane were formed, respectively. The addition product from bidiphenyleneethylene and benzylmagnesium chloride was found to behave as a Grignard reagent in its reaction with excess benzyl chloride. 1,2-Dibenzyl-1,2-bidiphenyleneethane was the product formed.

Such behavior made possible the proof that the Grignard reagent added in a 1,2 manner to the olefinic bond. When the addition product from bidiphenyleneethylene and benzylmagnesium chloride was caused to react with *p*-chlorobenzyl chloride, 1 - benzyl-2-*p*-chlorobenzyl-1,2-bidiphenyleneethane was produced. The same product was formed by the benzylation of the adduct from *p*-chlorobenzylmagnesium chloride and the olefin. The products would be identical only if the initial addition had taken place in a 1,2 manner to the central double bond.

Grignard reagents of lesser reactivity such as methylmagnesium iodide and phenylmagnesium bromide did not undergo addition to bidiphenyleneethylene nor did addition of *t*-butylmagnesium chloride or benzylmagnesium chloride take

place when benzalfluorene was employed as the olefinic hydrocarbon.

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VITA

The author was born in Silverton, Ohio, on August 9, 1924. He attended the public schools of Sycamore Township and was graduated from Sycamore Township High School in June, 1941. That fall, he entered Wilmington College at Wilmington, Ohio, where he held the departmental scholarship in chemistry for three years. He received the degree of Bachelor of Science in Chemistry from the above institution in July, 1944.

In the fall of 1944, he enrolled in the Graduate School of the University of Illinois where he held a teaching assistantship in the inorganic division until June, 1946. He was then employed by the Monsanto Chemical Company at Anniston, Alabama, for the summer. After his return to the University of Illinois, he held the Rohm and Haas research assistantship during 1946-1947 and a university fellowship during the summer of 1947.

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